1920
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M. J. Pearce

The Primary Decomposition Products of Fractional Carbonization of Illinois Coal

THE PRIMARY DECOMPOSITION PRODUCTS OF FRACTIONAL CARBONIZATION OF ILLINOIS COAL

BY

MARVIN JAMES PEARCE

THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CHEMICAL ENGINEERING

COLLEGE OF LIBERAL ARTS AND SCIENCES

UNIVERSITY OF ILLINOIS

1920

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DEGREE OF BACHELOR OF SCIENCE

IN CHEMICAL ENGINEERING.

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453025

ACKNOWLEDGMENT

The author expresses his indebtedness to Dr. T. E. Layng, upon whose suggestion this investigation was undertaken, and under whose direction it was carried out. A sincere appreciation is felt for the encouragement of independent work combined with the feeling that valuable suggestions would be offered when most needed.

TABLE OF CONTENTS

		Page
I	Introduction	1
	1 Nature of the Problem	1
	2 Previous Work on the Subject	2
	3 Outline of the Present Investigation	8
II	Experimental	9
	A Methods used in Experiments	9
	Temperature Measurements	9
	Analysis of Gases	9
	Determination of Water	12
	Determination of Tar and Oil	12
	Determination of Volatile Matter	13
	Apparatus Used	13
	Methods Used	15
	B Coal Used	16
	C Distribution of Products	17
	D Presentation and Discussion of Data	17
	Gases	17
	Tars and Oils	22
	Water	23
	Coke or Residue	24
III	Summary and Conclusions	25

TABLES

	Table	Page
Analysis of Coal	I	16
Products Liberated at 300° C	II	27
Yield of Products at Successive Temperatures	III	28
Composition of Gases, percent by Volume	IV	29
Volume of Gases at Successive Temperatures	V	30

FIGURES

	Figure	
Arrangement of Apparatus	I	31
Retort Used	II	31
Yield of Products at Successive Temperatures	III	32
Total Yield of Gas	IV	33
Volume of CH_4, H_2, CO_2, C_2H_6 at Successive Temps.	V	34
Volume of C_2H_4, C_6H_6, O_2 at Successive Temps.	VI	35
Volume of H_2S, CO, N_2 at Successive Temperatures	VII	38

THE PRIMARY DECOMPOSITION PRODUCTS OF FRACTIONAL CARBONIZATION OF ILLINOIS COAL

I INTRODUCTION

1. Nature of the Problem --- An exact knowledge of the behavior of the various constituents of coal upon heating is of primary importance wherever coal is used. In the manufacture of gas and coke, in the use of coal in boiler or metallurgical furnaces, or in any industrial application of coal or its products, the subject of carbonization is of paramount importance. Already we hear discussions as to the period of time that will elapse before the present store of fuel with which nature has supplied us will be exhausted. We may well ask ourselves if the present supply is being utilized to the best advantage. This question cannot be satisfactorily answered without understanding the nature of the reactions which occur when coal is heated.

Considerable data concerning the products derived from the destructive distillation of coal under ordinary conditions is available, but there is evidence that these products are the result of secondary decomposition and do not indicate the primary reactions which take place. Lewes (1) points out the fact that the ultimate products obtained are largely dependent upon external conditions such as temperature, rate of heating, time, pressure and contact surfaces. The purpose of the tests covered by this paper was to determine the primary products resulting from the

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(1) Lewes, V. B., The Carbonization of Coal p. 130 (1913)

carbonization of Illinois coal at successive temperatures with the exclusion of oxygen from the retort. The apparatus and methods used were planned to avoid secondary reactions as far as possible.

2. Previous Work on the Subject*--- Since 1902, investigations in the low temperature distillation of bituminous coals of the Illinois type have been carried on at the University of Illinois (1). It was found in a series of preliminary experiments that the percentage of fixed carbon could be increased by more than 25 percent with a corresponding decrease in the amount of volatile matter by heating coal for less than one hour at temperatures within the range of 250° to 500° C.

Later, Parr and Francis (2) used non-oxidizing atmospheres such as nitrogen and steam in order to eliminate variables due to oxidation. Coals heated in these inert media gave a residue which was smokeless and yet contained much of the volatile constituents. While using an atmosphere of steam, it was noticed that the temperature rose very abruptly at approximately 315° C. This phenomena has later been developed into a new theory for the coking of coals by means of exothermic reactions and a careful control of temperatures.

Parr and Barker (3) and Mahler and Charion (4) report that

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(1) Ill. Geol. Surv., Bull. No. 4, by S.W.Parr, p. 97 (1906)
(2) Bull. 24, Eng. Expt. Sta., U. of I. (1908)
(3) Bull. 32, Eng. Expt. Sta., U. of I. (1910)
(4) Compt. rend. pp. 150, 1521, 1604 (1910)

* Some references listed herein have been taken from Bull. No. 60, Eng. Expt. Sta., U. of I. and Tech. Paper 140, U.S. Bureau of Mines.

freshly mined coal gives off hydrocarbons and absorbs oxygen at relatively low temperatures. R. T. Chamberlain (1) also found that coal which had absorbed oxygen gives off a very small amount even under high vacuum. He advanced the theory that the oxygen entered into chemical combination with unsaturated compounds in the coal.

Burgess and Wheeler (2), working in England, distilled coal from a small platinum retort at temperatures ranging from 450° to 1100° C., and concluded from the results obtained that the point of secondary decomposition in coal is between 700° and 800° C. Increased quantities of hydrogen were evolved at this point. Later the same authors (3) distilled coal from a similar apparatus collecting samples of the gases evolved at given intervals. From the analysis of these fractions, they came to the conclusion that coal contained two types of compounds -- resinous substances which are relatively unstable and yield mostly hydrocarbons of the paraffin series; and humus or cellulosic substances which are more difficult to decompose and which yield mostly hydrogen. Clark and Wheeler (4) further substantiated this conclusion by separating coal into two parts by extraction with pyridene and chloroform. These separate parts were distilled and the products analyzed. In view of the recent work of Thiesen (5) on the microscopic sturcture of coal, resinous material should include resins, fatty acids

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(1) U. S. Geol. Surv. Bull No. 383 (1909)
(2) Jour. Chem. Soc., v. 97, pp. 1917-35 (1910)
(3) Jour. Chem. Soc., v. 99, pp. 650-67 (1911)
(4) Jour. Chem. Soc., v. 103, pp. 1705-15 (1913)
(5) Bull. 117, Bureau of Mines (1920)

waxes and their degredation products.

Porter and Ovitz (1) showed that the compositon of the volatile matter of coal depends largely upon the character of the coal itself. They found that the western coals gave higher percentages of the oxides of carbon than did those of the Appalachian region. From this, the writers concluded that the younger coals of the West contained compounds such as complex alcohols, aldehydes and acids. They further showed that Dulong was in error in assuming that all the oxygen of a coal combined with hydrogen during combustion.

Pictet and Bouvier (2) carried on a series of experiments in which they distilled coal under diminished pressure at 450° C with the exclusion of oxygen. The gases were not collected, but were passed through water, to which they gave an odor recalling butadiene and isoprene. The tars gave a marked petroleum odor, and contained no acids or other aromatic compounds. No ammonium compounds were obtained in any of the products collected. When a sample of the tar was distilled through an iron tube filled with coke and heated to redness, the following products were obtained: (a) a gas consisting chiefly of hydrogen and saturated hydrocarbons of the methane series, (b) a dark tar containing considerable amounts of phenol and (c) an oil from which were isolated benzene, napthalene and anthracene. From these experiments they concluded that the hydrogen and methane of illuminating gas, the ammonia of the ammonia liquors, and the phenols and aromatics of the tar are

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(1) Bull. 1, Bureau of Mines (1910)
(2) Compt. rend. 137, pp. 779-81 (1913)

not direct products of the dry distillation of coal, but are formed by secondary reactions between the original products.

The results obtained by V. B. Lewes (1) in 1911 further substantiate this theory. He states that the tar from a low temperature process contained much light oils, a high percentage of basic substances, small amounts of acids and aromatics, no napthalene, and a small amount of anthracene. Going back still further, G. E. Davis (2) states that low temperature tars consist chiefly of paraffins and olefins. He differs from Pictet and Bouvier and Lewes in the matter of the presence of phenols, however. At high temperatures, he maintains that the paraffins disappear almost entirely with the resultant deposition of carbon on the retort walls. The high temperatures also cause molecular condensations, forming napthalene, anthracene and other hydrocarbons of high molecular weight.

Parr and Olin (3), working with Illinois coal in an atmosphere of superheated steam, found that the gaseous products consisted chiefly of illuminants of high candle-power. They also found that about 20% of the nitrogen was liberated as ammonia at a temperature of 450° C. The liquid distillate consisted chiefly of unsaturated oils with the minimum amount of tar and free carbon. Later, these authors (4) found that tars from Illinois coal were rich in low boiling fractions and contained approximately 30% soft pitch. They contained high percentages of tar acids, but no

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(1) Iron and Coal Trades Review, v. 83, p. 1011 (1911)
(2) Jour. Soc. Chem. Ind., v. 5, p. 2 (1886)
(3) Eng. Expt. Sta., U. of I. Bull.60 (1912)
(4) Eng. Expt. Sta., U. of I. Bull. 79 (1915)

napthalene or anthracene.

Taylor and Porter (1) found that more than two-thirds of the organic substance of coal is decomposed at temperatures below 500° C. The older coals of the Appalachian region were found to be more difficult to break down than the younger coals of the middle-western and western fields. The first products of decomposition that appeared were water, carbon dioxide and carbon monoxide. Illinois coals were found to give off appreciable quantities of volatile matter below 250° C. The formation of paraffins, both liquid and gaseous, began at low temperatures, but proceeded very slowly at first. Below 400° C., paraffin hydrocarbon gases of the methane series, but higher than methane, predominated. The volatile matter was found to decompose readily at temperatures above 750° C., yielding permanent hydrocarbon gases and hydrogen. Hydrogen was found to predominate at temperatures above 750° C, even if secondary decomposition were prevented. The authors suggest that the yield of tar from a given coal could be doubled by reducing the temperature of distillation to 500° C. or less. The amount of water of decomposition was found to be greater below 500° C. than above. Hydrogen sulfide was produced at 250° C., and the amount rose rapidly as the temperature was increased. It was also found that the oxygen content of a coal determined to some extent the amount of water and tar that would be evolved. The percentage of coke was increased by slow carbonization.

From the foregoing reports, it will be seen that most investi-

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(1) U. S. Bureau of Mines, Tech. Paper 140 (1916)

gators agree that coal contains at least two chief types of matter -- resinous degredation products which are soluble in phenol, and yield mostly paraffins; and humic or cellulosic materials which are more difficult to decompose and yield mostly hydrogen. These materials are present in different proportions and in many types of degredation products which closely grade into one another. Good coking coals seem to contain a high percentage of resinous derivatives, and their humous derivatives are altered. The coking property of all coals can be destroyed by continued heating below their fusion point. This is probably accounted for by the alteration of the resinic derivatives present.

Furthermore, almost without exception, these investigators agree that the benzenes and paraffins of high carbon content are given off almost entirely at temperatures below 500° C. At higher temperatures, methane and hydrogen are the principal gas constituents, a part of them being derived directly from the coal and a part from secondary reactions among the primary products. The first products of decomposition to appear are the oxides of carbon and water. These are given off to some extent even at atmospheric temperatures.

Almost every authority states that the tars obtained from distilling coal at low temperatures contain a large percentage of low-boiling oils suitable for cleaning oils or for use in internal combustion engines. The amount of pitch present is very low, as is also the free carbon content. The yield of tar and oil is said by some to approximate twice the amount obtained at higher temperatures. Of particular interest is the fact that the low

temperature tars contain small percentages of aromatic compounds, phenol, anthracene and napthalene, while the paraffin oils seem to predominate. A rise in temperature tends to produce polymerization with the formation of more complex compounds of higher molecular weight.

3. Outline of the Present Investigation --- The present work concerns itself with a study of the primary volatile matter liberated from Illinois coal when subjected to distillation at low temperatures. The condensible and non-condensible gaseous products removed from the coal before secondary reactions can occur are referred to by the term "primary volatile matter". Briefly, the work done is covered by the following outline:

(A) Quantitative determination of the relative amounts of water, tar and gas liberated at 50° intervals between the temperatures 250° and 600° C.

(B) Determination of the type of compounds, and the amount of each present in the gases evolved at the various temperatures.

(C) Study of the rate of evolution of the volatile matter at different temperatures.

(D) Determination of the character of the tar with respect to its physical and chemical properties, whenever a sufficient quantity was obtained.

(E) Study of the results, as a whole, in order to determine, if possible, the type of coal constituent first decomposed, and what its resulting products are.

The effect of low temperature distillation upon the proximate and ultimate composition of the residue was not determined.

II EXPERIMENTAL

A. METHODS USED IN EXPERIMENTS

Temperature Measurements

Up to and including a temperature of 340° C. the temperatures were measured with ordinary nitrogen filled mercury thermometers. Above this point, calibrated thermoelements of iron and constantan (number 30 wire) were used with an Englehard millivoltmeter (Type P_1, No. 1941), connected in series with an 800 ohm resistance. The millivoltmeter was previously calibrated against a standardized platinum-rhodium (10 percent rhodium) thermocouple. The thermoelements were insulated, and protected from possible corrosive action of the liberated gases by means of silica thermocouple tubes. In all cases, two elements were used--one inside the retort, the other outside in the furnace--in order toobtain a more accurate control of the temperature at all times. Readings could be made within 2° C. It is well to state here that elements of copper and constantan failed to give satisfactory results, due to the rapid oxidation of the copper at the higher temperatures. This defect could have been reduced by using larger wires, but the thermocouples would have then become too large and cumbersome for the work in hand.

Analysis of Gases

The gases were collected and measured over water which had been saturated with NaCl. In order to further eliminate the absorption of any of the gases liberated, the water was also ex-

posed to quantities of coal gas obtained in previous experiments. The total volume of gases were calculated from the loss in weight of the container and the specific gravity of the salt solution. In some cases, where the quantity was small, the gases were measured directly in a Hempel gas burette, calibrated to one-tenth of one cubic centimeter. In all cases, the gas was at atmospheric pressure at the time of weighing or measuring. No attempt was made to correct the volumes to standard conditions of temperature and pressure. The methods employed in this investigation were too inaccurate in other respects to warrant this. The quantity of nitrogen added to the gases collected was determined by direct measurement in a gas burette.

A special form of apparatus which has been perfected at the University of Illinois was used in the analysis of the gases. This consists of a modified Orsat apparatus to which has been added a Hempel gas burette. An electric furnace for the determination of hydrogen and carbon monoxide, and a slow-combustion pipette for the determination of methane and its homologues also have been added. With this apparatus a complete analysis may be made with the same sample, without disconnecting any of the parts during the determination.

The carbon dioxide was determined by absorption in 40 percent KOH solution. The oxygen was removed by absorption in a solution of potassium pyrogallate, made by mixing equal volumes of a 1-3 solution of pyrogallic acid and a 40 percent solution of KOH. Sulphuric acid (89 percent) was used to absorb the unsaturated hydrocarbons of the ethylene series. Later a solution of

bromine, made by diluting one volume of saturated bromine water with two volumes of water, was substituted for the sulphuric acid solution. The bromine solution seemed to absorb the gases more rapidly, but it was found necessary to remove the bromine fumes by passing the gas into the KOH pipette before the volume was read. Members of the benzene series were absorbed by means of fuming sulphuric acid. As stated above, the hydrogen and carbon monoxide were determined by oxidation with copper oxide, heated to 300° C. The amounts of methane and ethane were estimated by means of the slow-combustion pipette method. From the equation $V = \frac{2C - A}{3}$, where V is the volume of hydrocarbons, C the contraction, and A the CO_2 produced, the relative amounts of methane and ethane present were calculated, as suggested by Abody (1).

By multiplying the percentages of the various constituents obtained by the above methods by the factor $\frac{G - N}{G}$, where G is the gas evolved and N the nitrogen added, the percentages on the nitrogen-free basis were determined. The sum of these percentages subtracted from 100 gave the percentage of nitrogen evolved. Since this method is subject to all the errors in the analysis, the percentage of nitrogen usually varies considerably. Fairly concordant results were obtained in this investigation, however.

The quantity of each gas evolved from 100 grams of coal was calculated from the total volume and the nitrogen-free percentages. The volume of H_2S and similar sulphur compounds was determined by means of slightly acid $Cu\ SO_4$, placed in the train leading from the retort to the gas container. The precipitate was filtered off and ignited, the volume of hydrogen sulphide being calculated

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(1) Gas Analyst's Manual, p. 356 (1902)

from the weight of CuO thus obtained. The filtrate was added to the water liberated by the coal, and the nitrogen determined by the Kjeldahl method. In no case was the ammonia found to be greater than one cc. per 100 grams of coal. This amount is so small, compared to the total volume of gas evolved, that the yield of ammonia has been given as zero at all the temperatures covered by this investigation.

The percentage composition of the total gas evolved was determined by dividing the volume of gas in question by the total volume, including that of the H_2S, and multiplying the result by 100.

The weight of the gases was calculated from densities given by Van Nostrand (1) in all cases except that of benzene. The weight of a liter of this substance was found by dividing its molecular weight by 22.3. The percentage of the original coal liberated as gaseous products was obtained by taking the sum of the calculated weights and multiplying the result by 100.

Determination of Water and Tar

Water and tar were condensed in a tube weighed before and after each test, and then poured into a 10 cc. graduated cylinder. By subtracting the volume of water from the total weight, the weight of tar evolved was approximated. A weighed calcium chloride U-tube was placed directly after the tar and water condenser to prevent moisture from escaping with the gas. This U-tube was protected from the Cu SO_4 solution by a second $CaCl_2$ tube. From

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(1) Van Nostrand's Chemical Annual (1913)

the total water produced during carbonization, the moisture determined by proximate analysis was deducted and the difference designated as water of decomposition.

In some cases, it was found difficult to separate the water and tar after pouring into the graduated cylinder. A fairly accurate determination was made on most of the tests, however. The percentage of paraffins contained in the tars was determined by the Babcock method, whenever possible. The results are only approximations, however, due to the small quantities available and to other difficulties which will be discussed later.

Determination of Total Volatile Matter and Residue

In some of the tests, the total volatile matter was determined by direct weighing of the retort and coal charge before and after heating; in others, the sum of the weights of water, tar and gas produced was designated as the total volatile matter. The amount of residue was determined by direct weighing in the earlier tests. At the higher temperatures it was determined by deducting the total volatile matter from the original weight of the coal.

Apparatus Used

The apparatus finally adopted for use in these experiments is shown in Figure I. The diagram is self-explanatory. At the lower temperatures, up to and including 400° C., the retort consisted of a 250 cc. Pyrex distilling flask. Above that temperature a cast iron retort, made of two inch gas pipe and fittings, was used. Figure II shows this retort. At first, some diffi-

culty was experienced in obtaining air tight joints. This trouble was finally eliminated by substituting two inch caps, suitably threaded, for the series of bushings formerly used. Dry nitrogen was admitted through A, and the gaseous and liquid products were removed through B. The temperatures were observed by means of a thermoelement placed in pocket C, extending into the mass of coal to be heated. Previously dried asbestos plugs were used to hold the charge in place and to prevent the outlet, B, from becoming contaminated with fine particles of coal. A gasket of thin asbestos paper, coated with a mixture of graphite and oil, was used to secure a tight joint between the flanges.

The source of heat was an electric furnace of the resistance type, wound with number 16 Chromel wire. The temperature was held under control at all times by means of a variable resistance, connected in series with the furnace. An ordinary 110 volt alternating circuit was used as the source of current. The rate of heating was held as near 75° C. per hour as possible. The temperature of the furnace rarely rose more than 100° C above the temperature of the coal. This sometimes occurred during the earlier stages of the heating, before the retort had reached the desired temperature.

The products evolved from coal are easily decomposed, if allowed to remain in contact with heated surfaces for some time. In order to prevent these secondary reactions, a vacuum of a few millimeters of mercury was used in all of the tests. By this means the liquid and gaseous products were quickly distilled from

the retort to cooler surfaces before sufficient time had elapsed for decomposition to occur. The vacuum was regulated by means of the aspirator bottles which were used as gas collectors. The amount of vacuum was determined by means of an open tube mercury manometer.

Operation

Before beginning the heating, pure, dry nitrogen was allowed to pass through the retort and train until the air was entirely displaced. The amount used varied from 800 cc. in the earlier tests to 2 or 3 liters at the higher temperatures. Nitrogen prepared by droping a saturated solution of NH_4Cl into a heated, saturated solution of $NaNO_2$ was first used. Difficulties were met in purifying the product, however, and commercial nitrogen, washed to remove oxygen and water vapor, was substituted.

During the heating, readings of the temperatures inside and outside the retort were taken every fifteen minutes. The resistance being used in the rheostat, the vacuum in the train, and the number of bubbles of gas per minute were also noted and recorded. A close check on the rate of evolution and other important data, such as the appearance of water and tar, was afforded by this means.

After holding the coal at the desired temperature until the evolution of gas had approached zero(the time varied from 1 to 4 hours, depending upon the temperature), the apparatus was swept out with a measured volume of nitrogen. Then the stopcock just above the $CuSO_4$ solution was closed and the retort allowed to cool

to room temperature. The contraction of a volume of nitrogen, connected with the retort during its cooling process, was taken as indicating the volume of nitrogen driven into the gas receiver during the heating of the retort.

B. COAL USED

Table I gives the data concerning the coal used in these tests. A quantity of air dry coal (about 3000 gms.) sufficient for the entire series of experiments, was ground to pass a 100 mesh sieve at one operation by means of a ball mill, and sealed in glass containers to prevent a change in moisture content. In the earlier experiments, 100 grams of coal was used for each test; later, this amount was reduced to 50 grams.

TABLE I

Composition of Coal

	Air-Dry	Moisture-Free
Moisture	4.10%	
Ash	8.03%	8.35%
Sulphur	1.99%	2.07%
Volatile Matter	34.01%	35.42%
Fixed Carbon	53.86%	56.11%
Total Carbon	73.20%	75.80%
Hydrogen	4.15%	4.32%
Oxygen	7.53%	7.84%
Nitrogen	1.50%	1.56%
B.t.u.	12,660	13,188

Unit B.t.u. = 14,564

C. DISTRIBUTION OF PRODUCTS

The very complex nature of coal makes it impossible to obtain exactly the same series of reactions in two different tests made under approximately the same conditions of temperature, rate of heating, pressure, and so forth. It is to be doubted, if check data could be obtained even with the external factors exactly under control, since it is entirely impossible to arrange the coal constituent particles in the same manner for each test. The variation in the distribution ratio of the main products of decomposition at 300° C is shown in Table II. Since it is impossible to obtain check results at a given temperature, all data given hereafter, unless otherwise stated, has been compiled from the averages of two or more tests made at each temperature.

Table III shows the ratio of distribution of the main products of decomposition at the various temperatures. This data is shown graphically in Figure III.

D. PRESENTATION AND DISCUSSION OF DATA

Gases

Percentage composition of the gases evolved at successive temperatures is given in Table IV. Table V shows the volume of each constituent per 100 grams of coal. The data is presented graphically in Figures IV, V, VI and VII.

From Figure IV, it will be seen that some decomposition takes place below 250° C. Rapid evolution of gas first begins, however, between 300° and 350° C.

Carbon dioxide and water are probably the first products of decomposition, judging from the slope of the curves at 250° C (Figures III and V). These products are followed, in the order named, by carbon monoxide, methane and its homologues, ethylene and its homologues, benzene and its homologues, and hydrogen, as the temperature is increased (Figures V, VI and VII).

The fact that the products first appear in this order, leads to the formulation of the following theory concerning the primary decomposition of Illinois coal:

Oxygen compounds, probably of the fatty acid type, are the first to be decomposed, yielding chiefly CO_2 and water. Later some CO appears as the scarcity of oxygen increases. As the temperature is raised, methyl, ethyl and other aliphatic groups begin to split off with the formation of methane, ethane and higher paraffins. This would leave unsaturated chain compounds behind. As the temperature is still further increased, some of these unsaturated compounds distill off and form hydrocarbons of the C_2H_4 type; another part of them may be condensed into more stable aromatic compounds. This would probably cause the evolution of hydrogen to take place. It will be noticed from Figures V and VI that benzene and hydrogen begin to be evolved at about the same temperature. If the temperatures were carried above those used in these tests, no doubt we would find an increased yield of hydrogen and aromatic compounds for a period up to 750° to 800° C. Then, as the temperature is further increased, we would probably find the yield of hydrogen still increasing, while the aromatic

compounds would be condensed into ring structures of high molecular weight, with the subsequent deposition of free carbon.

It must be understood that these reactions do not occur in separate distinct stages with the exclusion of all other reactions. The very complex nature of coal makes it impossible to control conditions in such a way as to obtain only one reaction at a time. This theory is offered to show the tendency toward decomposition and to explain the order in which the products begin to appear. No doubt, the products mentioned above are liberated from many other compounds than those of the fatty acid type. This particular type of compound was chosen as an illustration upon which to base the general theory that carbon is more stable toward carbon than toward oxygen or hydrogen when subjected to an increase in temperature. That is, the molecules tend to become more compact as the temperature increases.

The curve for benzene is the most peculiar of the entire set. (Figure VI). A maximum is reached at 450° C. Above this temperature, the volume declines rapidly. There are two factors which may account for the peculiar shape of the curve. It will be remembered that bromine water was substituted at this temperature for 79 percent sulphuric acid as an absorbent for ethylene. It may be that the sulphuric acid failed to remove all the ethylene, some of it being absorbed by the fuming sulphuric acid, along with the benzene. This would cause those determinations below 400° C to be too high in benzene. Or, the explanation may lie in the fact that some of the benzene was absorbed by the increased quantities of tar above 400° C., and thus be eliminated from the gas.

It will be noted that the volume of oxygen liberated is constant until a temperature of 450° C has been passed (Figure VI). Above this temperature, the volume begins to increase. This increase is probably due to inaccuracy in analysis, however. It is easy to appreciate the fact that an error of a few hundreths of one percent in the analysis would make quite a variation in the calculated volume of oxygen, if it is remembered that the total volume of gas at the higher temperatures is several thousand cubic centimeters.

For some time it has been known that freshly mined coal will give off volatile matter and take up other gases, showing a preference for oxygen. It is also known that coal which has been subjected to an atmosphere of oxygen for some time, will fail to give up all the oxygen which it absorbed, even if it is placed under a heavy vacuum (1). The question that remains to be decided is, does the oxygen enter into chemical combination with the coal or is it simply adsorbed. The fact that it is difficult to liberate oxygen which has once been taken up by coal seems to indicate that something stronger than physical bonds are needed to hold the oxygen so firmly. Nevertheless, the fact that a constant volume of oxygen was obtained in these experiments shows that at least some oxygen must be present in coal simply as an occluded gas. The other explanation possible is that the oxygen is loosely held in organic compoundswhich break up easily. It is hardly probable that this is the case, however. A more likely explanation is that

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(1) R.T.Chamberlain, Bull. 383, U.S. Geol.Surv. (1909)

a part of the oxygen is chemically combined and a part held as an occluded gas. A series of experiments are now being devised by Dr. T. E. Layng of the University of Illinois, to determine the manner in which oxygen is held in coal.

Hydrogen sulphide is given off in small quantities below 300° C., but it is at this temperature that rapid evolution begins. (Figure VII). As pointed out by Parr and Olin (1), the hydrogen sulphide liberated at low temperatures must be a decomposition product of organic sulphur compounds, since the decomposition point of FeS_2 is 750° C and above. A series of experiments on the residues left from the tests described in this paper is to be conducted by Mr. Charles C. Russell, under the direction of Professor S. W. Parr, to determine the amount and type of sulphur compounds remaining after low temperature carbonization.

As explained in an earlier part of this paper, the amount of H_2S liberated above 450° C was estimated, after it was found that there seemed to be a reaction with the hot iron of the retort.

Since nitrogen is determined by difference, it is subject to all the errors of analysis. This may account for the sudden increase in volume at about 325° C. Since the volume is practically constant before and after this temperature, however, it seems more likely that some of the nitrogen held in the coal is liberated as such at this temperature. More work needs to be done on the subject before a definite conclusion can be drawn, however.

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(1) Bull. 60, Eng. Expt. Sta. U. of I., p. 10 (1912)

Tars and Oils

By referring to Table III, it will be seen that the yield of tar approximates 50 percent of the total volatile matter given off by the coal. There was some trace of oil at 250° and 300° C., but a quantity sufficiently large to be determined was not obtained till 350° C. From this point up, the yield of tar gradually increased until a temperature of 550° C was reached. The high percentage obtained at 500° C is probably due to some residual tar from the previous test being left in the delivery tube of the retort. Above 550° C, the yield seems to decrease slightly, probably due to some of the tar vapors being decomposed into permanent gases by the high temperatures.

The tars showed a tendency to separate into two portions, one lighter and the other heavier than water. The heavy portions seem to be given off at the higher temperatures, and constituted 10 to 20% of the total yield. Because of this separation of the tar and lighter oils, it was difficult to obtain the yield exactly. Very close approximations were obtained, however, by subtracting the volume of water collected from the combined weight of tar and water.

As mentioned before, an attempt was made to determine the amount of paraffins present, by means of the Babcock test. Some difficulty was experienced in the determination, due to the paraffins being mostly of a solid nature. It was found necessary to warm the tar and acid slightly, in order to get a separation. The paraffin compounds approximated 10 percent of the tars at all the

temperatures above 350° C. No attempt was made to determine the acid or phenol content of the tars, since a sufficient quantity was not obtained.

When first distilled, the tars were of a translucent reddish nature. Upon standing, they were easily oxidized to a dark brown or black color. They also showed marked drying qualities, leaving a thin, hard, gelatinous film-covering. This suggests their use as a vehicle in paint mixtures, varnishes and drying oils.

Water

It is quite generally conceded that when oxygen compounds of coal decompose, water is formed. This is commonly known as water of decomposition or water of constitution. It is to be noted that some decomposition of this nature takes place even at a temperature of 250° C. The amount of water produced continues to increase till a temperature of 400° C has been reached, after which it remains almost constant. Carbon dioxide and carbon monoxide seem to be the other products of the decomposition of the oxygen bearing compounds.

At this point, it might be of interest to note that while making tests at 250° C., an apparent back pressure was created in the retort when the temperature had reached 120° C. This phenomenon was first observed by the writer when he returned to the laboratory after a short absence and found that the $CuSO_4$ solution had been sucked back into the $CaCl_2$ tube, although the temperature of the furnace had shown a rise in temperature. It was decided to notice this portion of the test more in detail, in order to

discover a cause for this peculiar action. In eight of eleven tests made at this temperature the phenomenon was found to exist in different degrees. This back pressure was found to continue until the coal had reached a temperature of 190° C., at which point decomposition began to take place. It appears that this behavior might be the result of two causes: either the rapid condensation of water vapor in the system or the absorption of nitrogen by the coal. Since most of the hygroscopic water had been driven off before this temperature was reached, indications point toward the latter explanation. A more thorough investigation of the subject should be made, however, before any definite explanation is offered. At higher temperatures, where the rate of heating through this period was more rapid, no back pressure was noted.

Coke or Residue

In none of the tests was the coal found to fuse together to form a coke. The particles of coal began to adhere to each other at 450° C., however, and from this point up the residue gradually assumed a structure more like that of coke. At 600° C. the residue had become quite compact, but could still be broken apart with the fingers. The failure to coke is probably due to the slow rate of heating to which the coal was subjected.

III SUMMARY AND CONCLUSIONS

The data obtained during the present investigation on the primary volatile products of Illinois coal at successive temperatures may be summarized as follows:

1. Two samples of a given coal exposed to the same external conditions of temperature, pressure, rate of heating, etc., may yield different amounts of volatile products and coke, and the composition of these products may vary, due to the arrangement of the constituents of the mass of coal.

2. Volatile matter begins to distill in appreciable quantities from Illinois coal at temperatures below 350° C. Water and carbon dioxide are given off in measurable quantities at temperatures as low as 190° C. These products, together with H_2S and CO and oxygen are the first to be liberated when Illinois coal is subjected to fractional carbonization. They result from the breaking down of oxygen bearing substances, probably degradation products of the cellulosic and fatty acid constituents of coal.

3. The oxygen compounds are almost entirely decomposed at temperatures below 450° C. This is proved by the fact that constant volumes of water and carbon dioxide are obtained above this temperature.

4. Methane and other members of the paraffin series are the next products of decomposition to appear. Ethane and the higher members of this series are present in the greater proportion at the low temperatures. As the temperature is increased up to 600° C, the relative percentage of methane is also increased.

5. Unsaturated hydrocarbons of the C_2H_4 type begin to be liberated at 300° C., and their amount increases as the temperature rises. Their presence may be explained by the theory that organic substances of the fatty acid type have been decomposed into unsaturated compounds, with the liberation of water, CO_2, CO and paraffin hydrocarbons, such as methane and ethane.

6. Sulphurétted hydrogen is liberated at temperatures as low as 250° C., although it first appears in large quantities above 300°C.

7. A constant volume of oxygen is liberated at all the temperatures covered by this investigation. No explanation is offered for this phenomenon, other than the theory that oxygen must be present in the original coal in two forms: one as oxygen-containing substances, the other as an occluded gas.

8. The volume of nitrogen evolved takes a sudden rise at 350° C. Below this temperature and above 450° C the volume is constant.

9. An apparant back pressure is found to exist between the temperatures of 120° C and 190° C. A tentative explanation is that coal has a strong affinity for nitrogen, in the absence of oxygen, during this range of temperatures.

10. The tars liberated at temperatures covered by this investigation consist of two portions, one lighter and the other heavier than water. The lighter fraction makes up approximately 80% of the total yield, and shows marked drying qualities. The tar fraction contains approximately 10% of paraffins, most of which exist inthe solid state at room temperatures. All of the tar has been evolved at 500° C., the greatest yield being obtained at this temperature.

TABLE II

Products of Illinois Coal at 300° C.

	Experiment Number		
	13	14	15
Duration, hrs.	1.25	3.00	2.50
Temperature, °C	294-300	290-310	290-310
Weight of Coal, air-dry, gms.	100	100	100
Total Loss, gms.	5.03	5.78	5.49
H_2O of Decomposition, %	1.00	1.23	1.13
Tar, %	trace	trace	trace
Gas Evolved, %	0.27	0.23	0.22
Gas per 100 grams of coal: (cubic centimeters)			
CO_2	93.00	120.00	132.10
O_2	53.20	38.10	37.60
C_2H_4	1.10	5.47	5.40
C_6H_6	0.0	5.47	0.00
H_2	0.0	0.0	2.72
CO	26.10	20.16	13.10
C_nH_{2n+2}	56.00	33.60	55.90
N_2	53.50	58.20	25.82
H_2S	2.50	3.60	3.33
NH_3	0.00	0.00	0.00
Total	285.40	284.60	279.00
Composition of gas: (percent)			
CO_2	32.60	42.18	47.40
O_2	18.60	13.36	13.50
C_2H_4	0.38	1.96	1.94
C_6H_6	0.00	1.96	0.00
H_2	0.00	0.00	9.75
CO	9.20	7.06	5.78
C_nH_{2n+2}	19.70	11.79	20.08
N_2	18.75	20.20	9.28
H_2S	0.88	1.26	1.20
NH_3	0.00	0.00	0.00

TABLE III

Yield of Products at Successive Temperatures

Temperature °C:	250	300	350	400	450	500	550	600
Duration, hours	2.00	2.50	3.00	3.75	3.00	3.00	3.00	4.50
Wt. of Coal, air-dry, gms.	100	100	100	100	50	50	50	50
Total Water, grams	4.70	5.23	6.55	6.72	3.45	3.35	3.36	3.35
Moisture, grams	4.10	4.10	4.10	4.10	2.05	2.05	2.05	2.05
Water of Decomposition, %	0.60	1.13	2.45	2.62	2.80	2.60	2.62	2.60
Tar, percent	trace	trace	1.96	6.00	7.00	13.80	12.00	11.10
Gas, cubic centimeters	143.70	280.70	829.60	2750.0	2760.5	3591.5	4677.5	5201.5
Gas, percent	0.24	0.43	0.94	3.11	5.98	6.92	9.08	9.54
Total Loss, percent	4.63	5.49	8.70	17.10	19.90	23.32	27.38	26.76
Coke Residue, percent	95.37	94.51	91.30	82.90	80.10	76.68	71.62	73.24

TABLE IV

Composition of Gases Evolved at Successive Temperatures
(Percent by Volume)

Gas	250° C	300° C	350° C	400° C	450° C	500° C	550° C	600° C
Carbon Dioxide, CO_2	46.2	41.0	21.7	14.7	22.8	13.1	15.0	13.1
Oxygen, O_2	30.3	15.3	2.3	1.5	0.7	0.7	0.7	0.7
Ethylene, C_2H_4	0.0	1.4	2.6	4.8	3.8	4.3	3.1	2.9
Benzene, C H	0.0	0.6	3.1	3.3	2.6	0.7	0.7	0.3
Hydrogen, H_2	0.0	0.3	7.7	9.2	17.0	24.8	22.8	25.0
Carbon Monoxide, CO	9.0	7.4	6.3	2.6	2.8	4.0	4.1	4.9
Methane, CH_4	0.0	17.3	18.2	16.5	14.2	22.2	32.5	33.9
Ethane, C_2H			8.9	22.6	18.1	13.7	6.6	6.4
Nitrogen, N_2	14.8	16.3	5.1	12.8	7.5	5.6	4.8	3.2
Hydrogen Sulfide, H_2S	trace	0.4	24.0	11.9	10.4	10.9	9.8	9.6
Ammonia, NH_3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total	100.3	100.0	99.9	99.9	99.9	100.0	100.1	100.0

TABLE V

Volume of Gases Evolved at Successive Temperatures
(Cubic Centimeters per 100 grams of Coal)

Gas	250°C	300°C	350°C	400°C	450°C	500°C	550°C	600°C
Carbon Dioxide, CO_2	66.2	115.0	180.0	405.0	1275.0	940.0	1400.0	1360.0
Oxygen, O_2	43.4	42.9	19.3	42.4	39.5	50.5	61.3	75.2
Ethylene, C_2H_4	0.0	3.9	21.8	131.0	211.5	311.0	285.8	300.0
Benzene, C H	0.0	1.8	25.6	91.0	145.0	50.5	61.3	32.8
Hydrogen, H_2	0.0	0.9	63.6	254.0	950.0	1780.0	2135.0	2598.0
Carbon Monoxide, CO	12.9	20.8	52.5	71.6	158.5	287.0	387.5	506.0
Methane, CH_4	0.0	48.5	151.0	452.0	793.5	1600.0	3032.0	3525.0
Ethane, C_2H	0.0		74.2	622.0	1010.0	985.0	620.0	670.0
Nitrogen, N_2	21.2	45.8	42.1	353.0	418.0	399.0	453.0	336.0
Hydrogen Sulfide, H_2S	trace	1.1	199.5	326.0	*580.0	*780.0	*920.0	*1000.0
Ammonia, NH_3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total Yield	143.7	280.7	829.6	2750.0	5581.0	7183.0	9355.0	10403.0

* Estimated

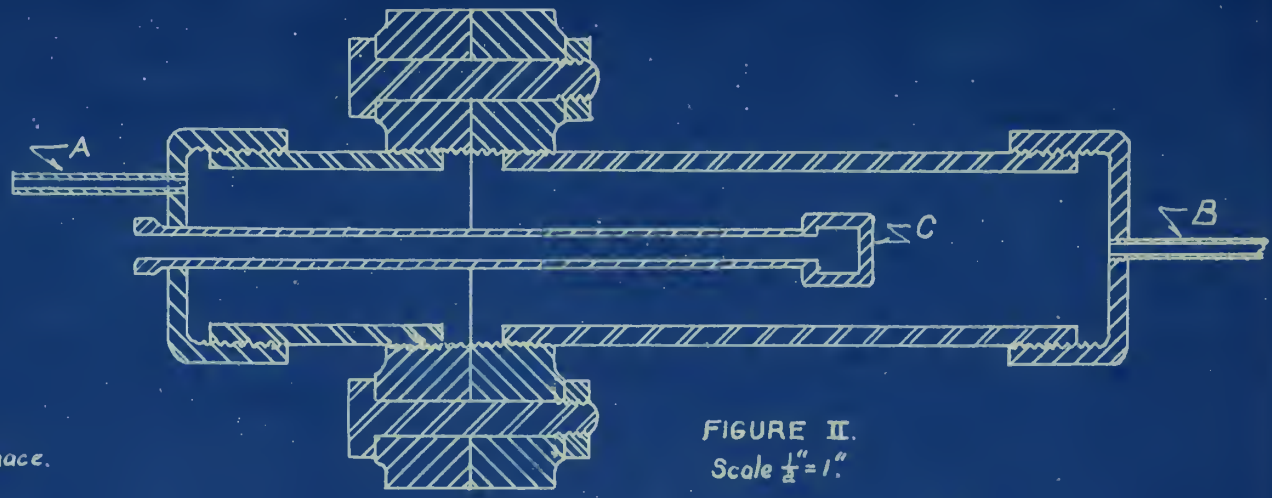


FIGURE II.
Scale $\frac{1}{2}$" = 1".

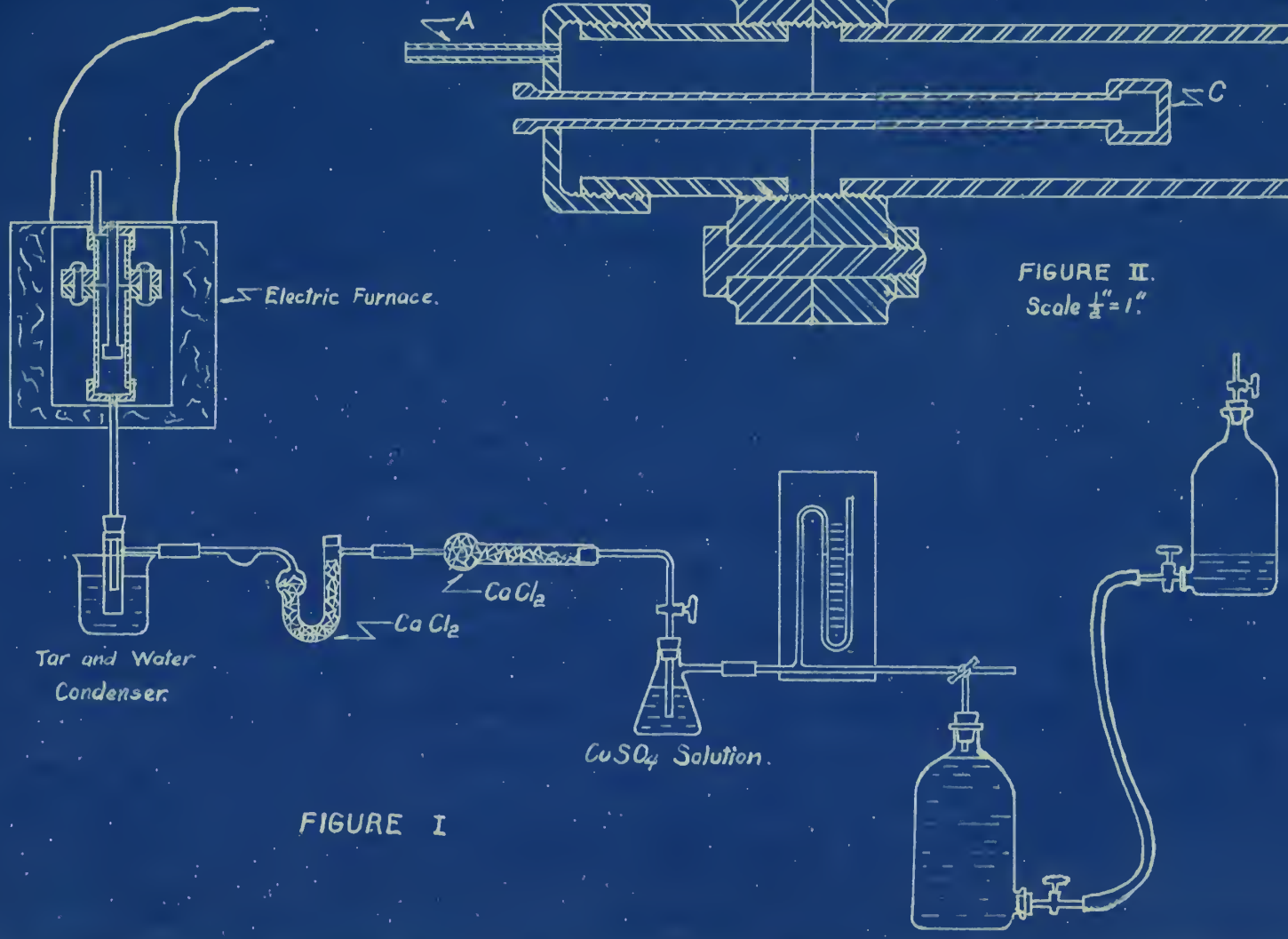


FIGURE I

FIGURE III

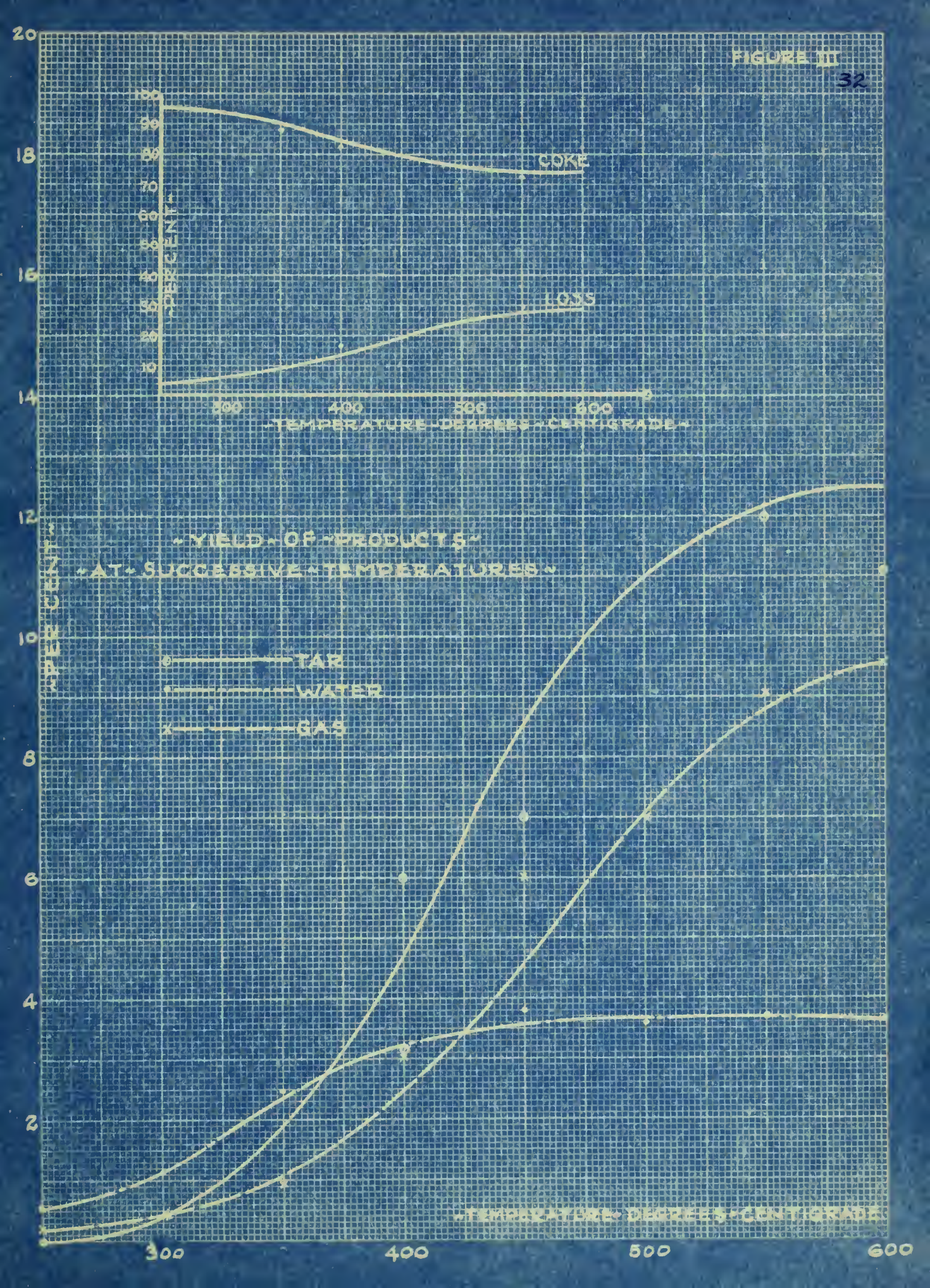

COKE
LOSS
TEMPERATURE DEGREES CENTIGRADE
"YIELD" OF "PRODUCTS"
"AT" SUCCESSIVE "TEMPERATURES"
TAR
WATER
GAS
INTERVAL DEGREES CENTIGRADE
300
400
500
600

FIGURE IV

TOTAL YIELD OF GAS FROM ILLINOIS COAL AT SUCCESSIVE TEMPERATURES

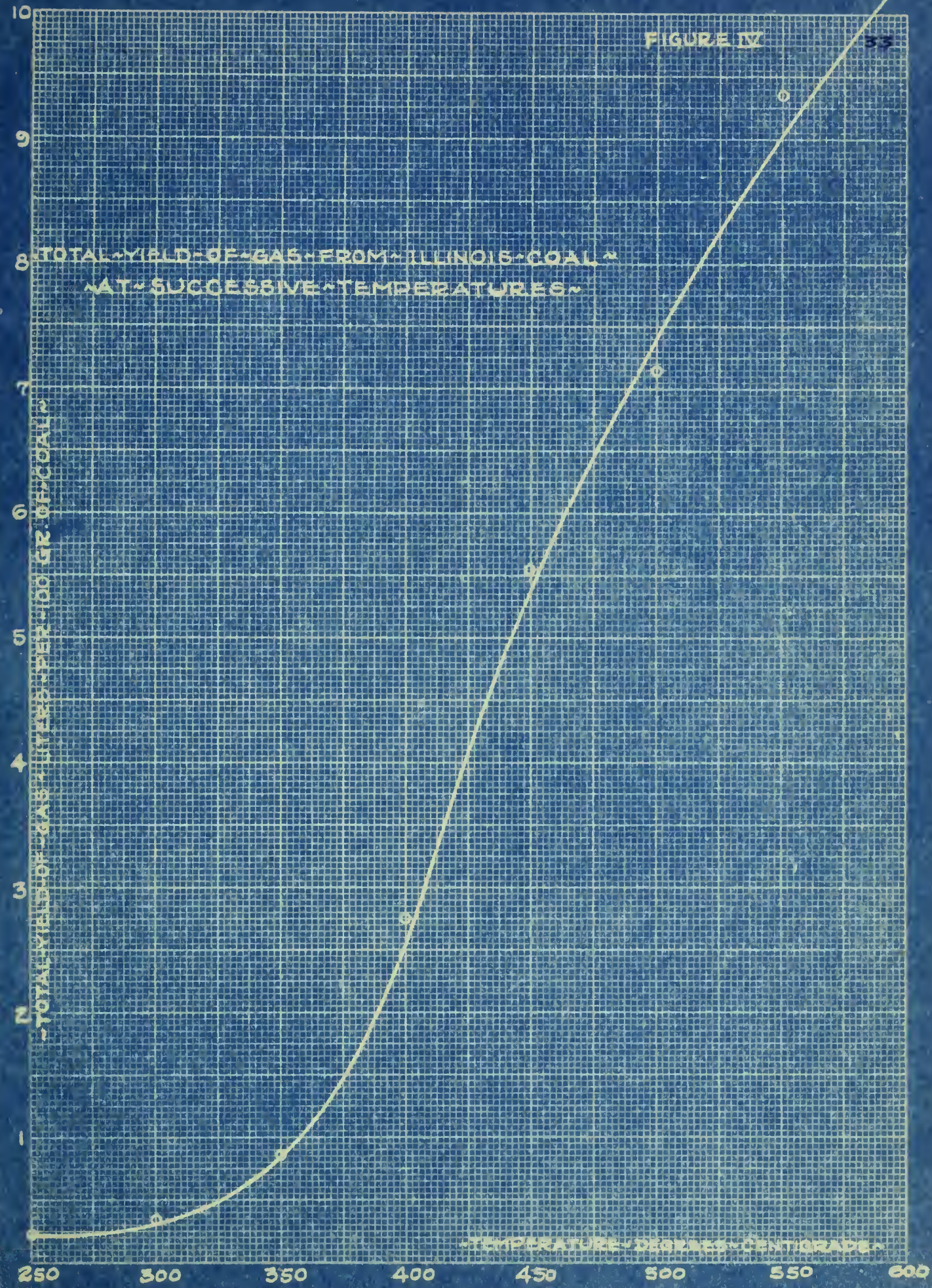
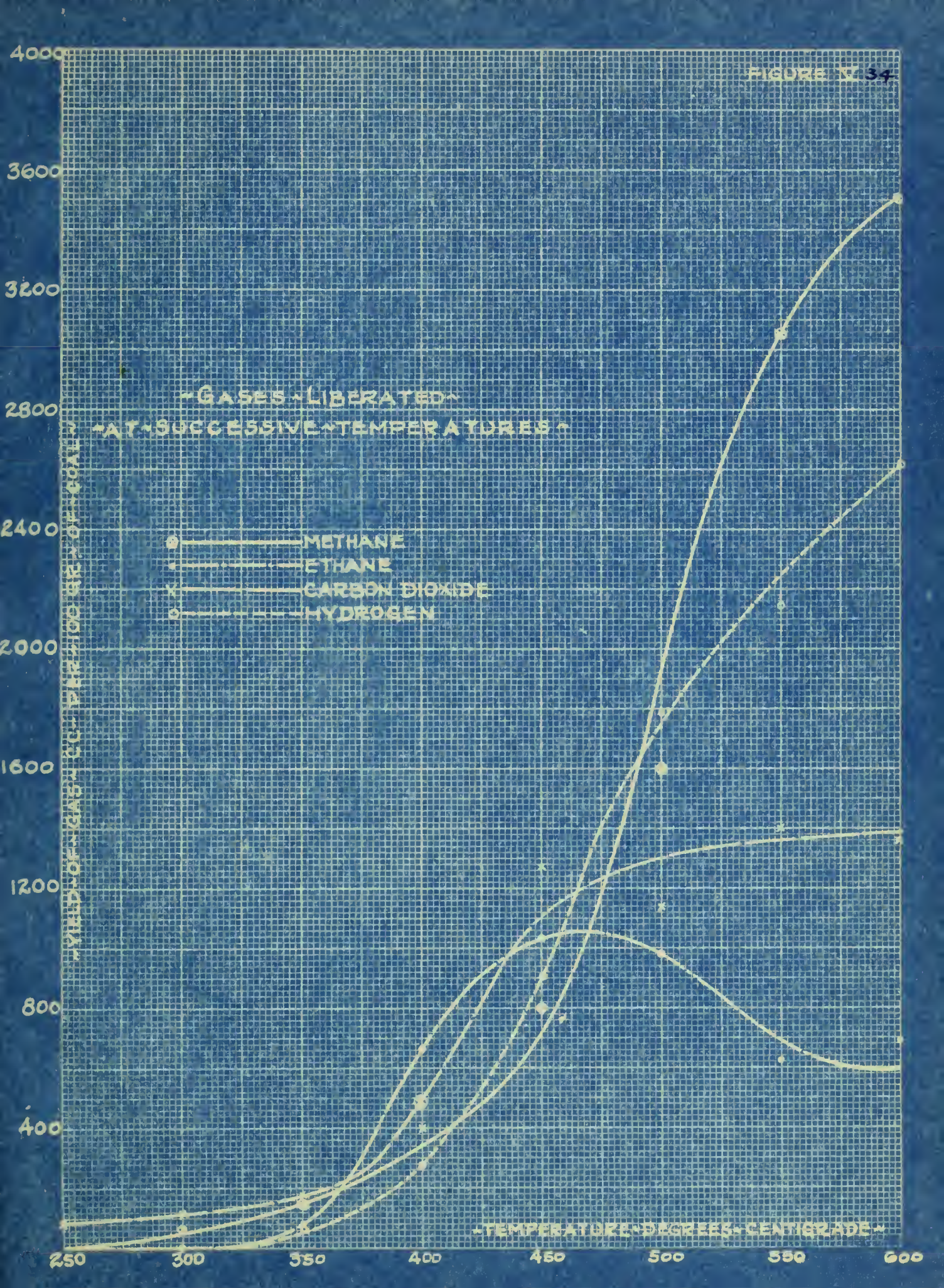


FIGURE V. 34.


GASES LIBERATED
AT SUCCESSIVE TEMPERATURES
METHANE
ETHANE
CARBON DIOXIDE
HYDROGEN
YIELD IN CUBIC CENTIMETERS PER GRAM OF COAL
4000
3600
3200
2800
2400
2000
1600
1200
800
400
250
300
350
400
450
500
550
600
TEMPERATURE DEGREES CENTIGRADE

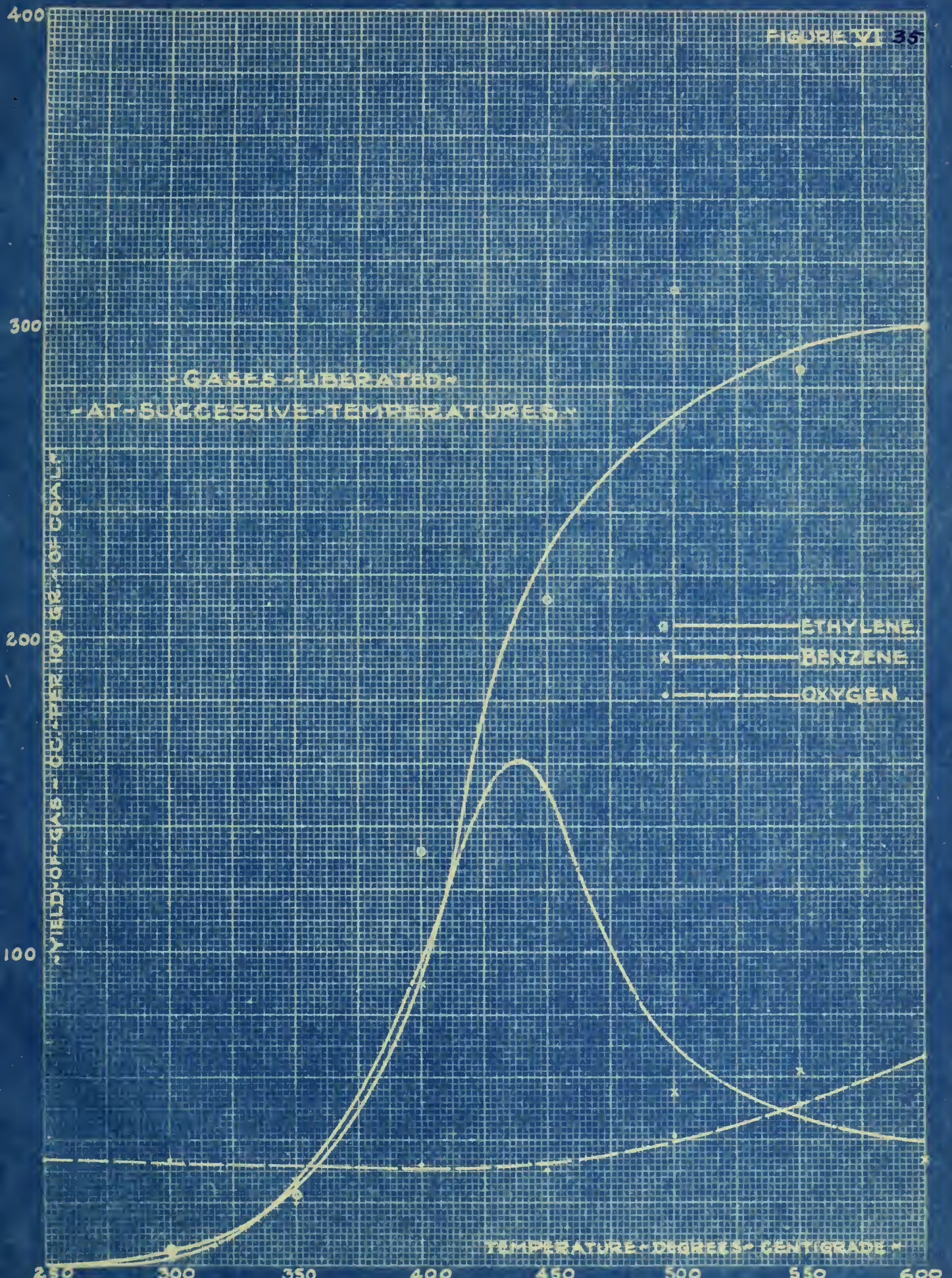
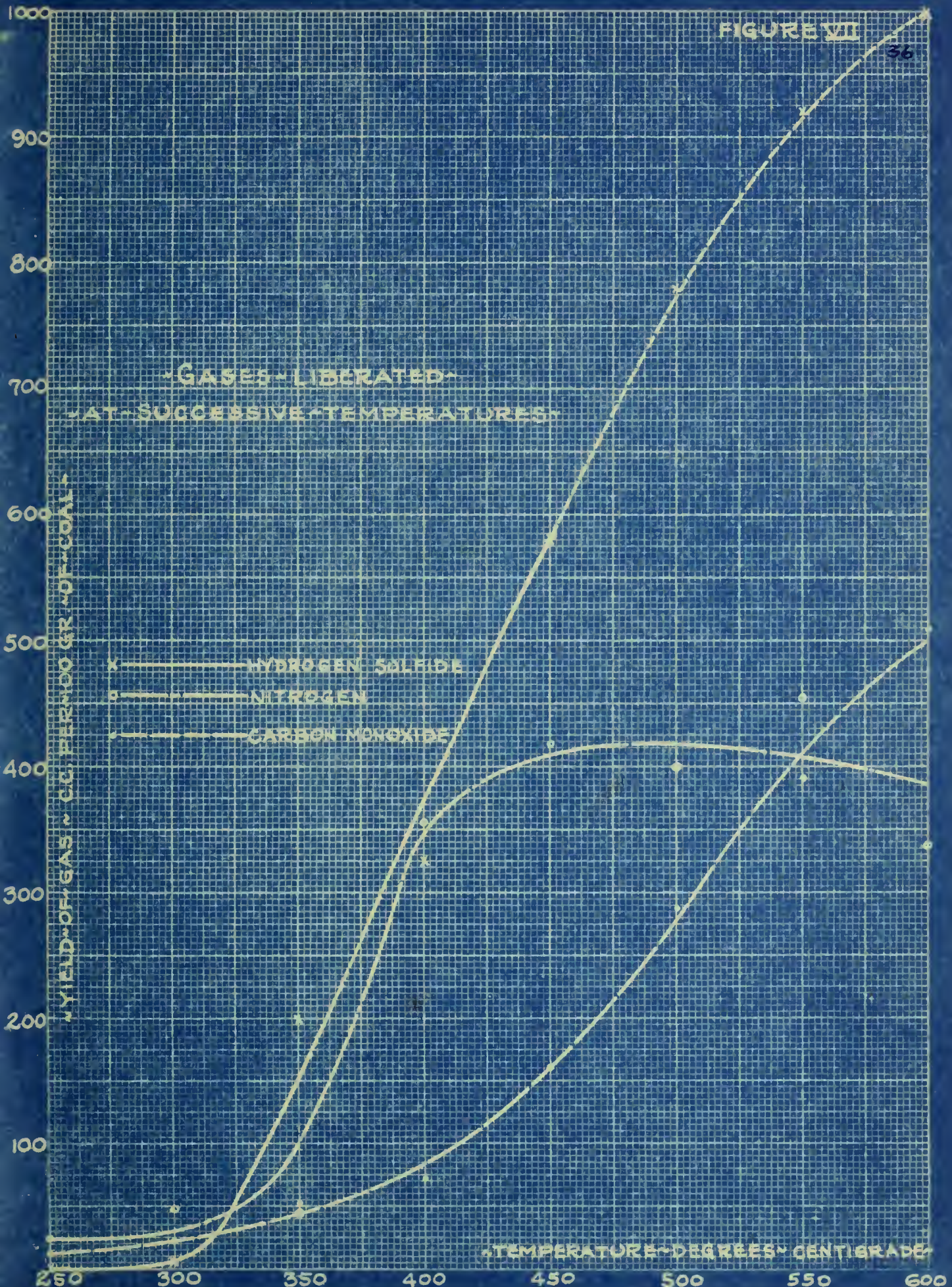


FIGURE VI 35
GASES LIBERATED
AT SUCCESSIVE TEMPERATURES
YIELD OF GAS IN CUBIC CENTIMETERS PER 100 GRAMS OF COAL
ETHYLENE
BENZENE
OXYGEN
TEMPERATURE DEGREES CENTIGRADE
400
300
200
100
250
300
350
400
450
500
550
600

FIGURE VII


GASES LIBERATED
AT SUCCESSIVE TEMPERATURES
YIELD OF GAS IN C.C. PER GRAM OF COAL
HYDROGEN SULFIDE
NITROGEN
CARBON MONOXIDE
TEMPERATURE DEGREES CENTIGRADE
1000
900
800
700
600
500
400
300
200
100
250
300
350
400
450
500
550
600

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